Simultaneous Measurements of Carbon, Hydrogen, Nitrogen, Sulfur, and Oxygen with Thermal/Optical Analysis

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Motivation

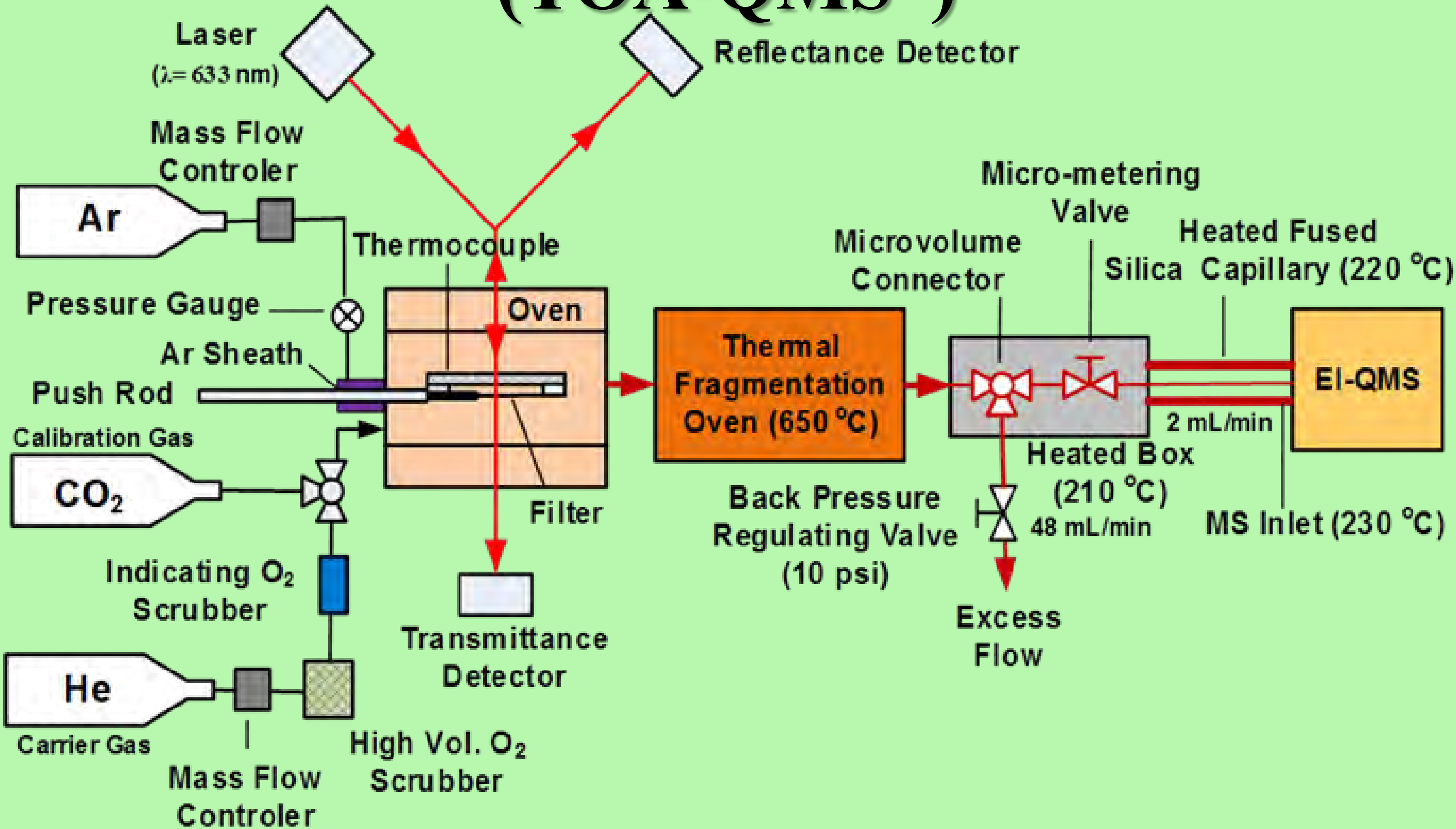
- More than 100,000 thermal/optical analyses (TOA) are performed worldwide on quartz-fiber filters each year, including long-term trends networks in the U.S., Canada, and China
- It is desirable to obtain more information from these analyses beyond simple carbon fractions (e.g., organic and elemental carbon [OC and EC]) at no added cost
- New developments in detector technology show potential for expanding the components quantified by thermal methods

Objectives

- Identify approaches for expanding thermal analysis from carbon (C) to hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) and their associated compounds

- Demonstrate that the long-term OC/EC trends record can be maintained by detector modifications

Approach 1: Emulate the AMS for filters (TOA-QMS*)



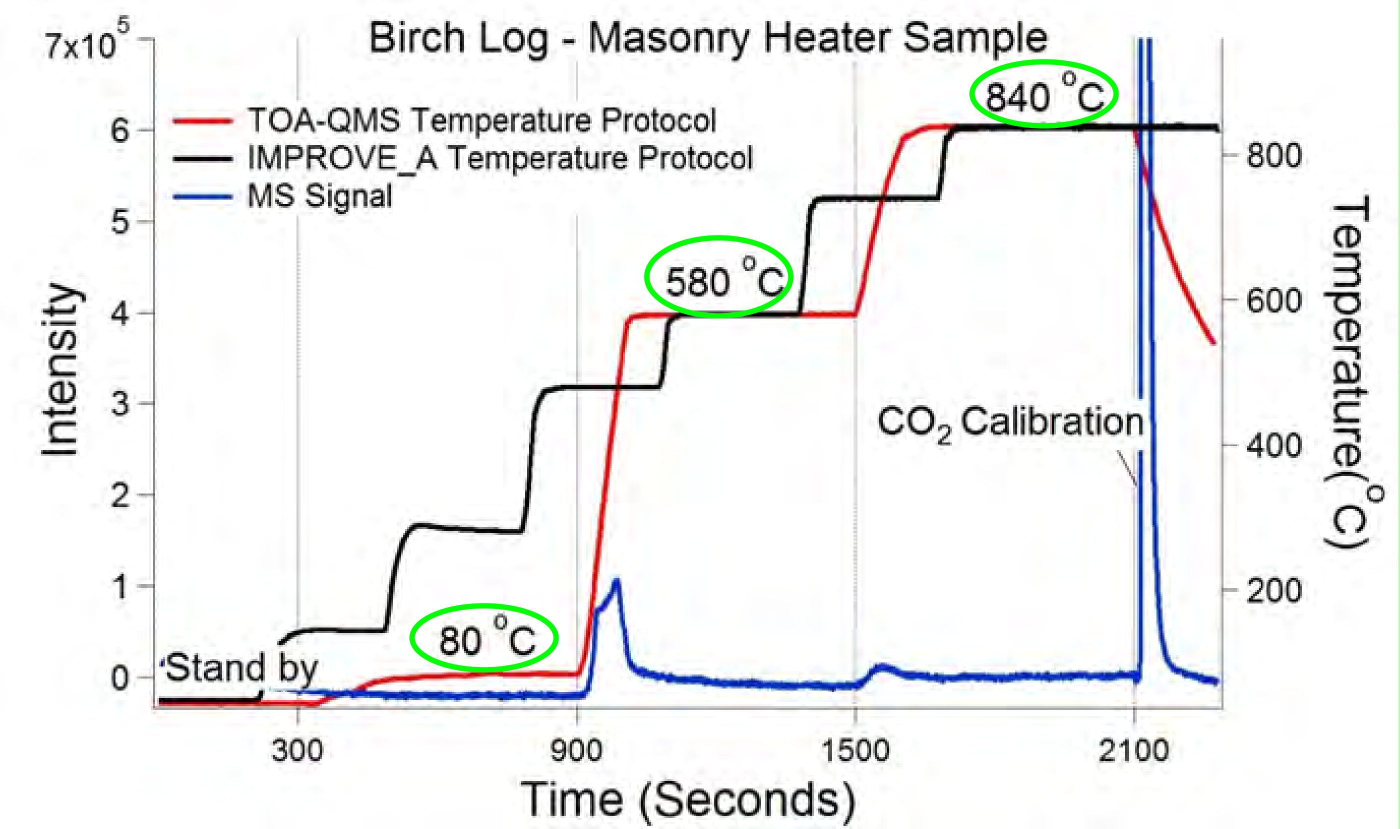
*TOA-QMS: Thermal/Optical Analyzer with Quadrupole Mass Spectrometry

Riggio, G.M. (2015). Development and application of thermal/optical- quadrupole TOA-QMS mass spectrometry for quantitative analysis of major particulate matter constituents., M.S. Thesis, University of Nevada Reno, Reno, NV.

The IMPROVE temperature program is simplified for testing

Temperature Steps (in helium atmosphere):

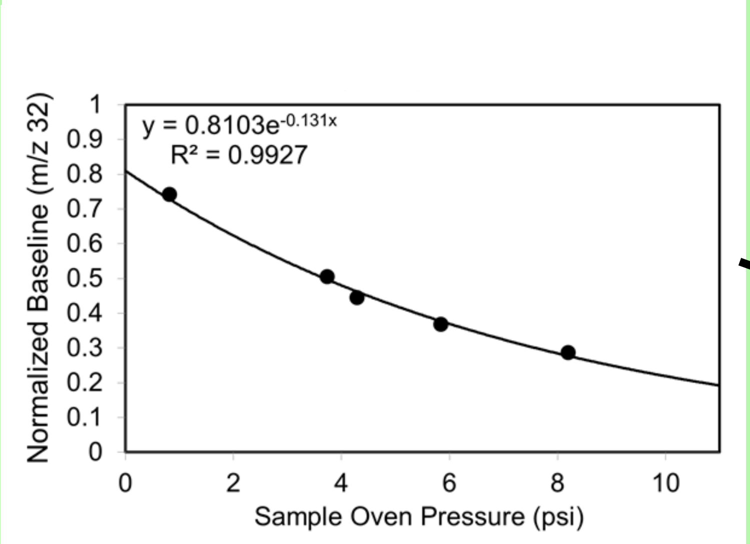
- 80 °C – Desorption of H_2O
- 580 °C – Combustion of most species (OC4 of IMPROVE_A)
- 840 °C – Combustion of remaining species (EC3 of IMPROVE_A)



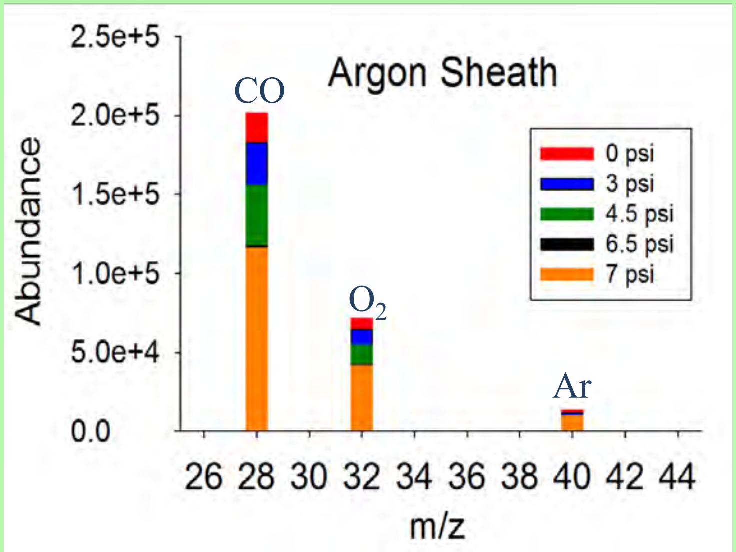
Chow et al. (2007). The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database. *J. Air & Waste Manage. Assoc.* **57**:1014-1023.

Air infiltration during sample insertion is reduced with higher pressure and an argon sheath

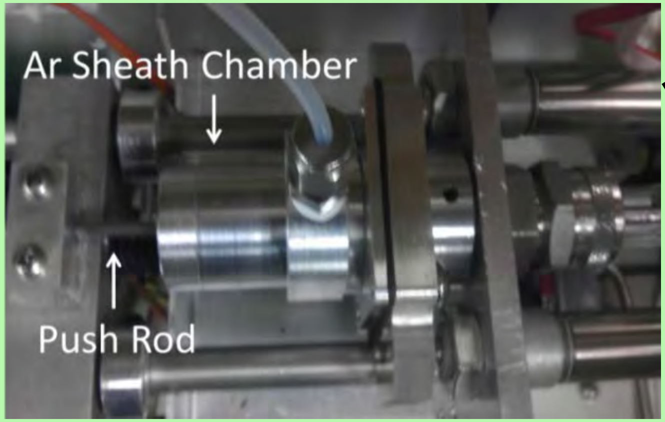
Increase sample oven pressure from 5 to 10 psi



Reduce O_2 from 15.5 to 8.5 ppm

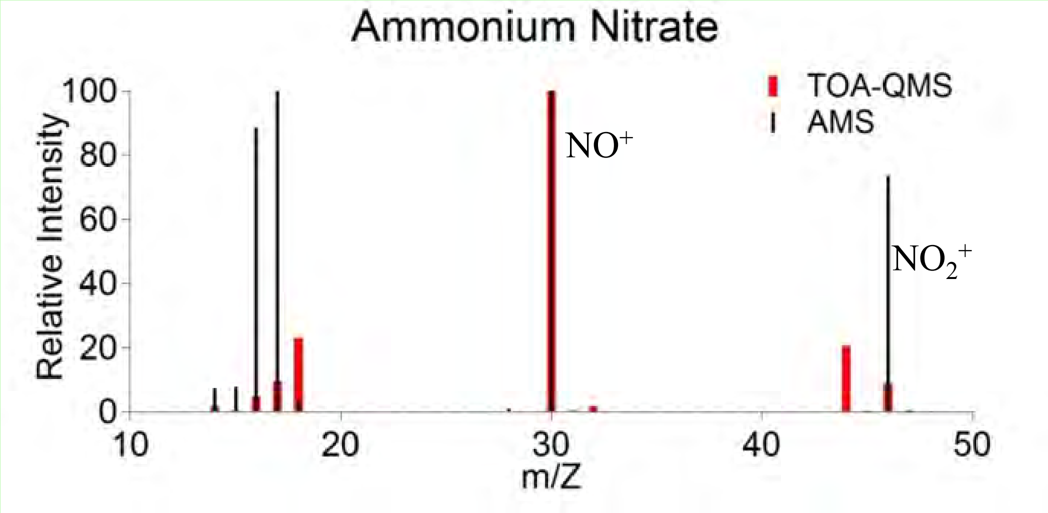


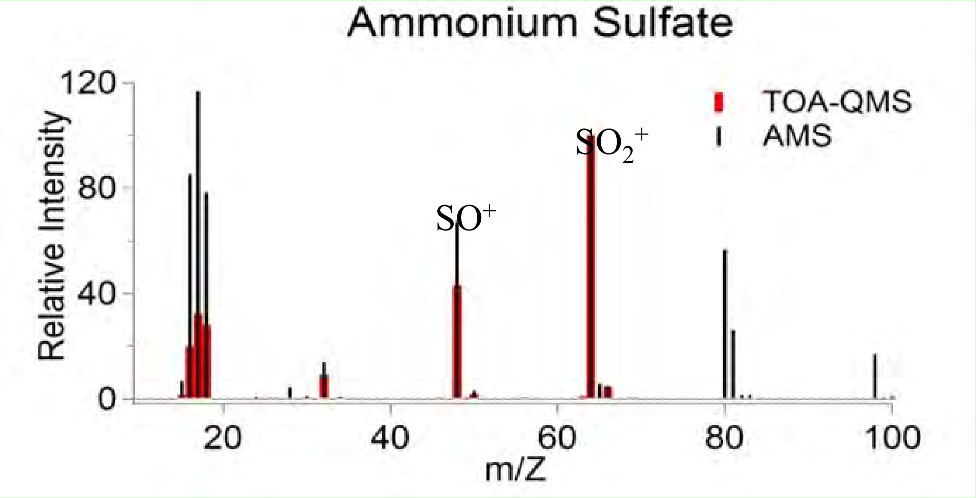
Argon sheath chamber



TOA-QMS spectra are similar , but not identical, to AMS spectra

- Potential causes of differences
  - -Heating rate
  - -Particle collection medium
  - -Thermal desorption
  - -Ionization

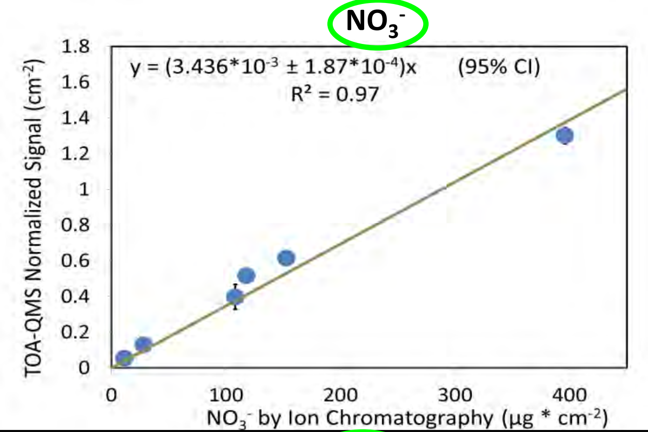


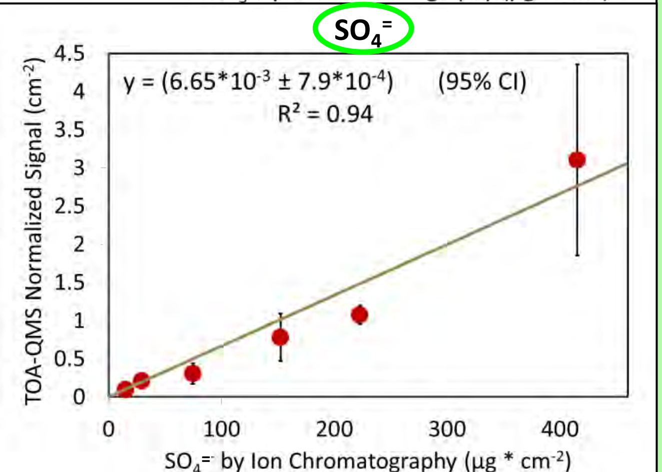


AMS Spectra from:

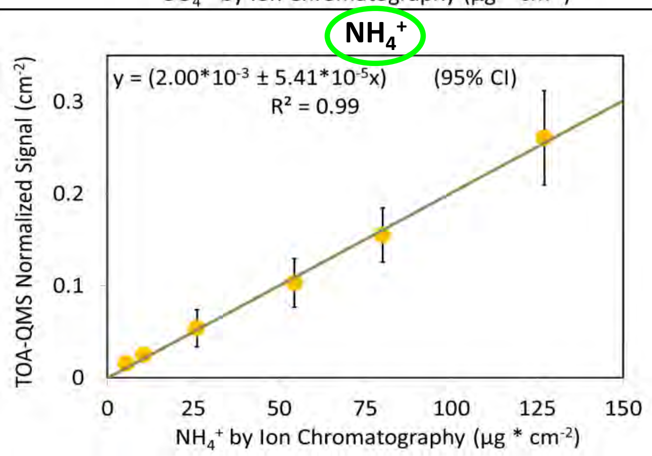
Allan et al. (2004). A generalised method for the extraction of chemically resolved mass spectra from aerodyne aerosol mass spectrometer data. *J. Aerosol Sci.*, **35**(7):909-922.

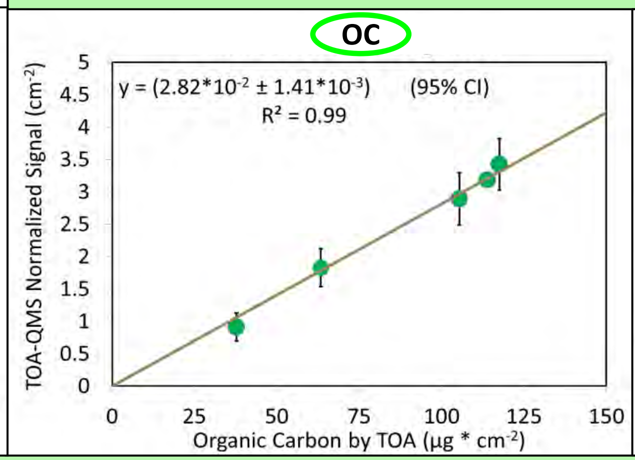
Jimenez et al. (2003). Ambient aerosol sampling using the Aerodyne aerosol mass spectrometer. *J. Geophys. Res.*, **108**(D7):doi:10.1029/2001JD001213.

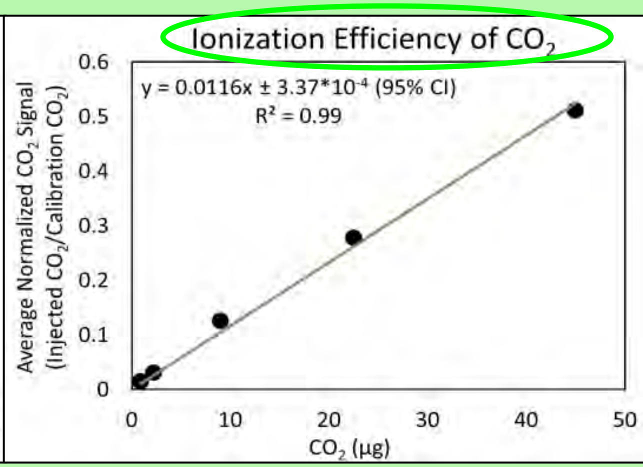




Signal/response is determined by analysis of quartz filter samples of nebulized NH_4NO_3, $(NH_4)_2SO_4$, and oxalic acid solutions.

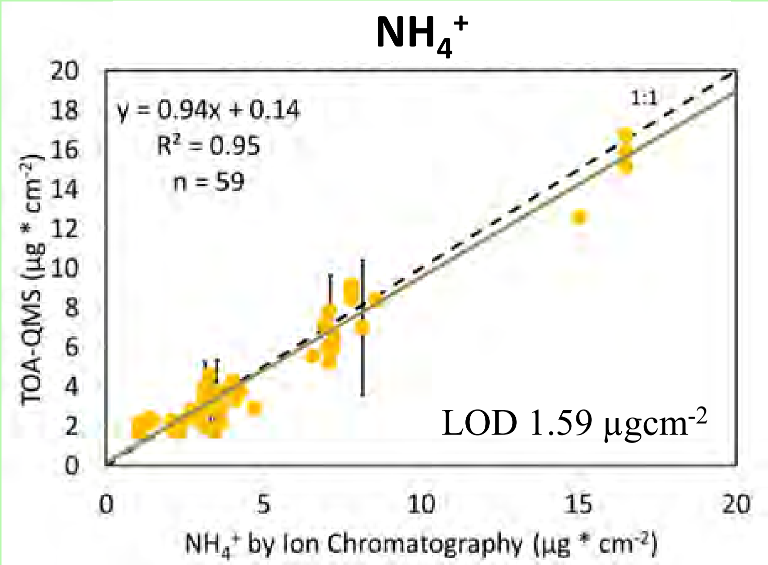


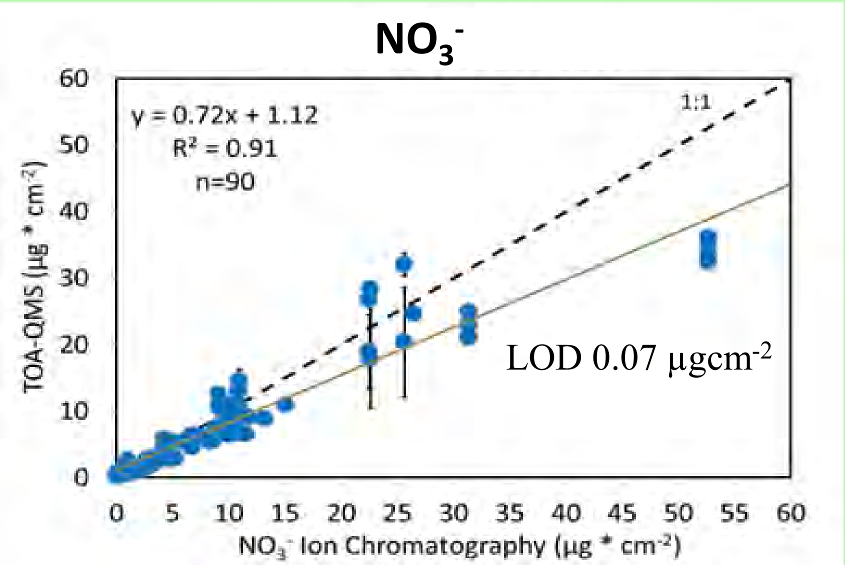


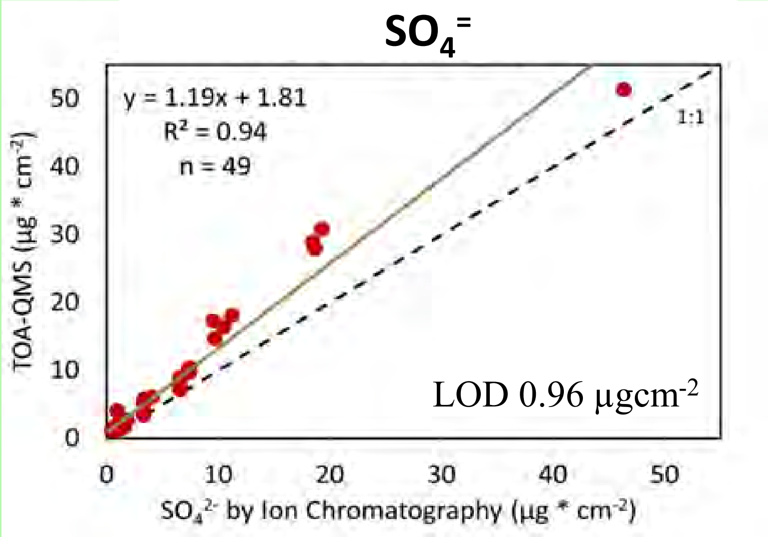


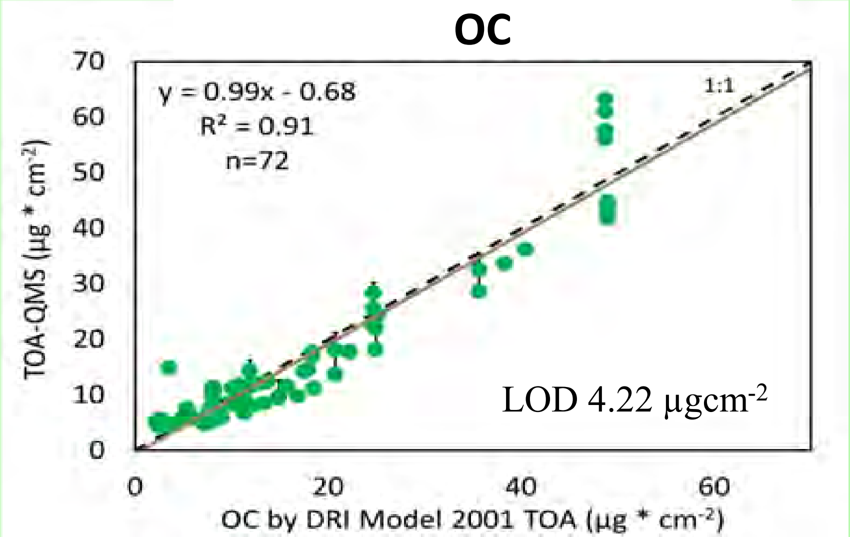
Application to ambient samples shows good correlation, but systematic biases

(58 Fresno, CA, samples; Dec 2000 – Feb 2001)



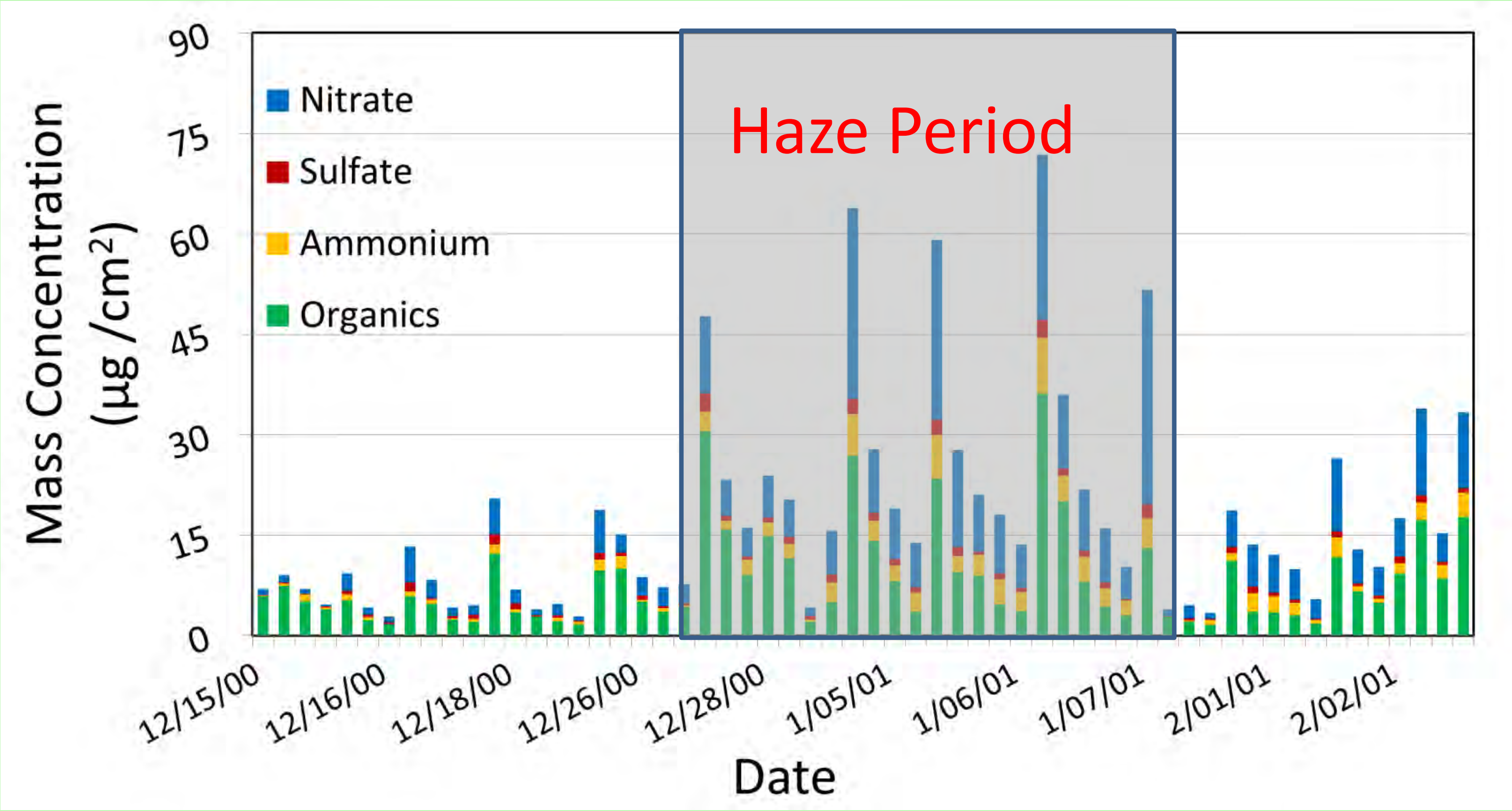






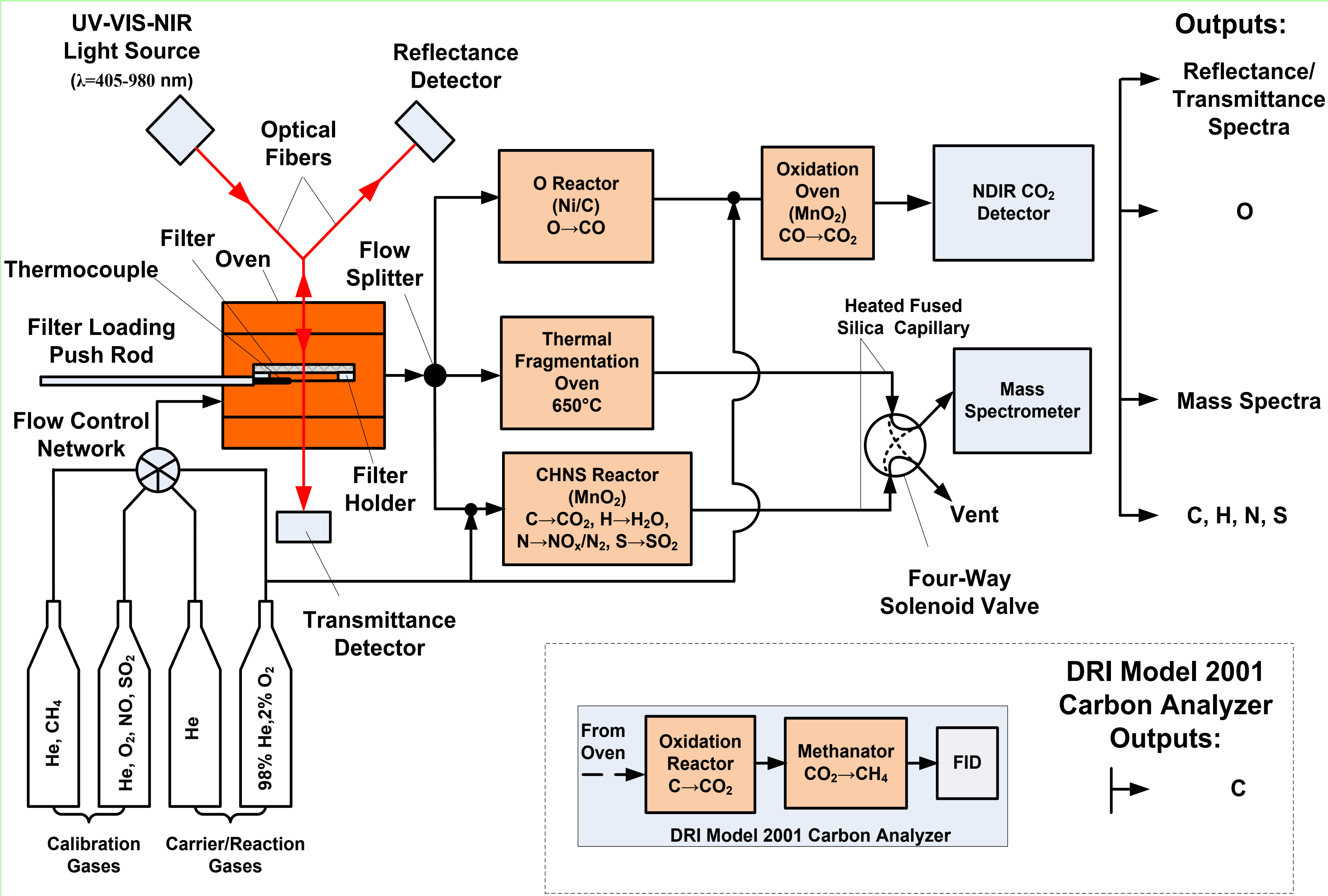
Concentration variations are similar to those obtained from speciation analyses

(Fresno supersite, 58 samples; Dec 2000 – Feb 2001)

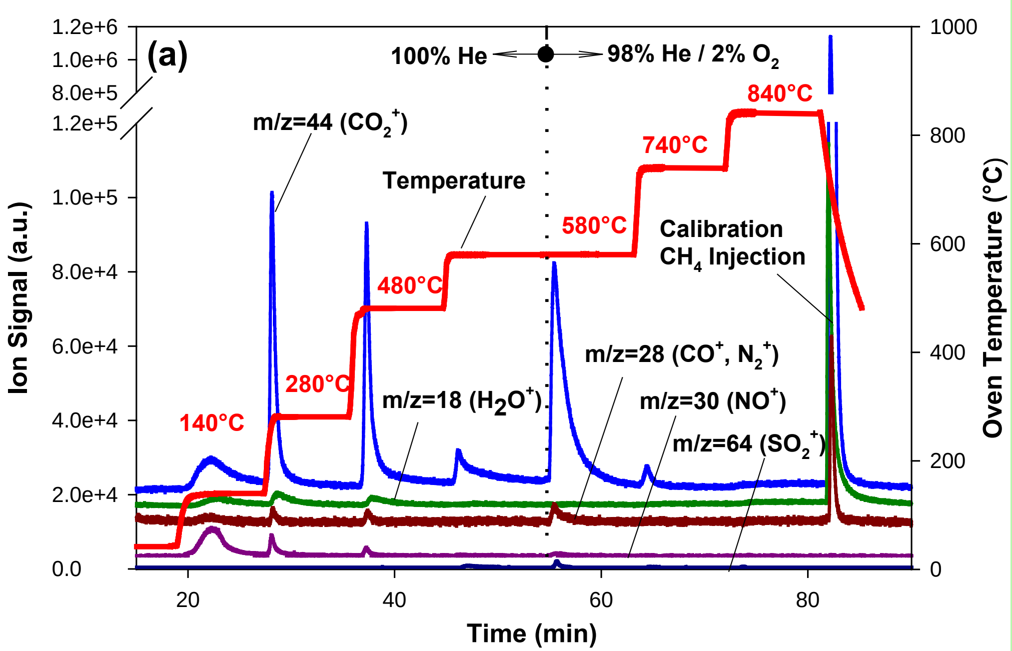


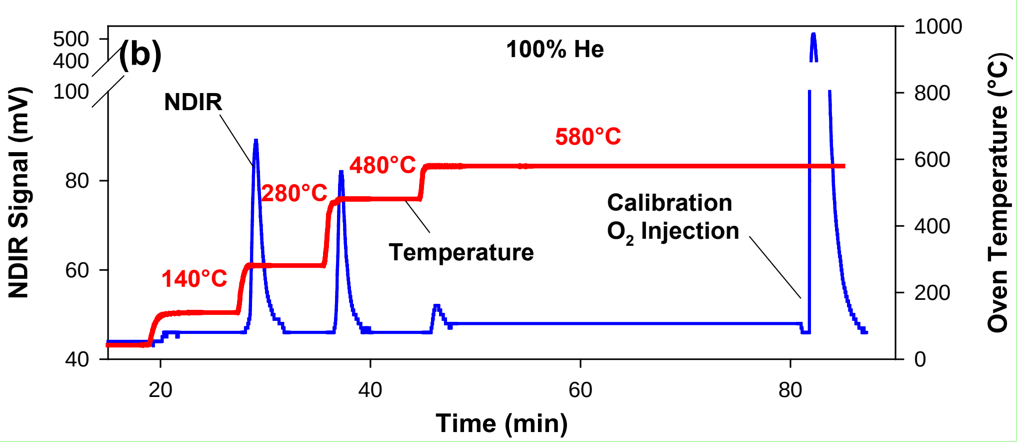
Largest concentration of species between 16:00 and 24:00 Local Standard Time

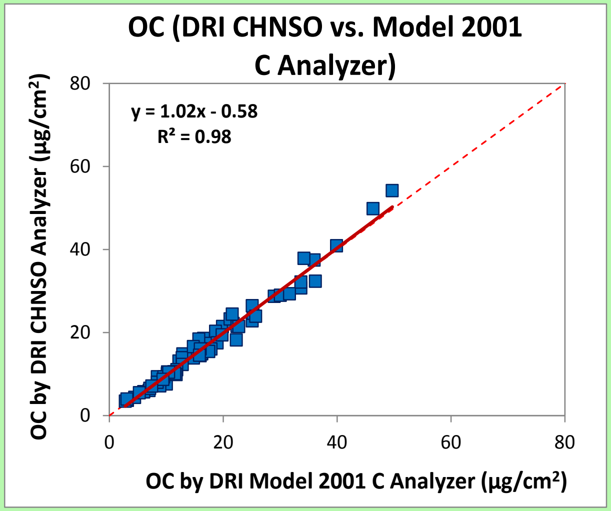
Approach 2: Oxidize thermally-evolved products to simpler compounds (TOA-O-QMS/NDIR)

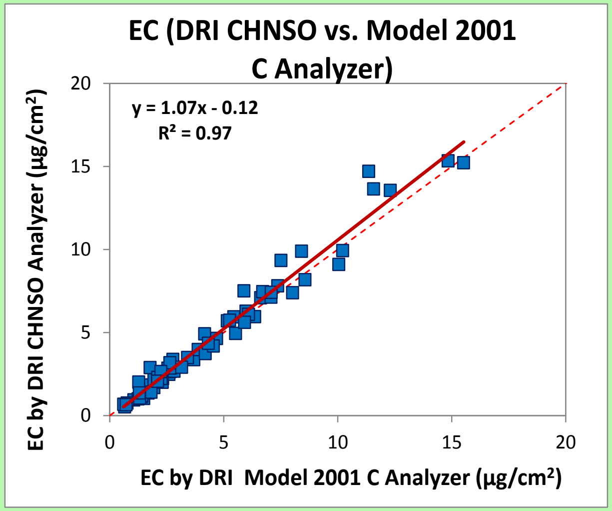


Existing thermal/optical protocols can be adapted to quantify C, H, N, S, and O



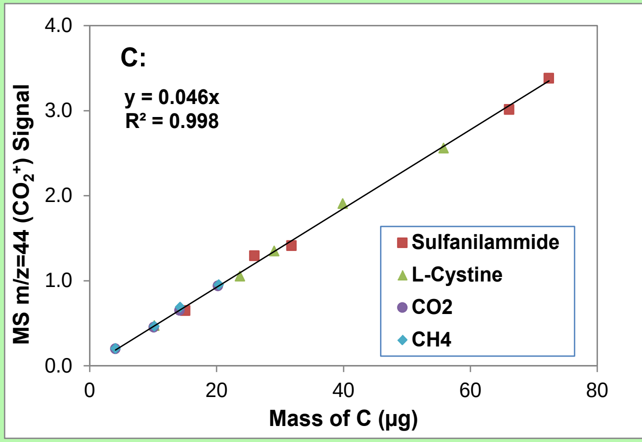


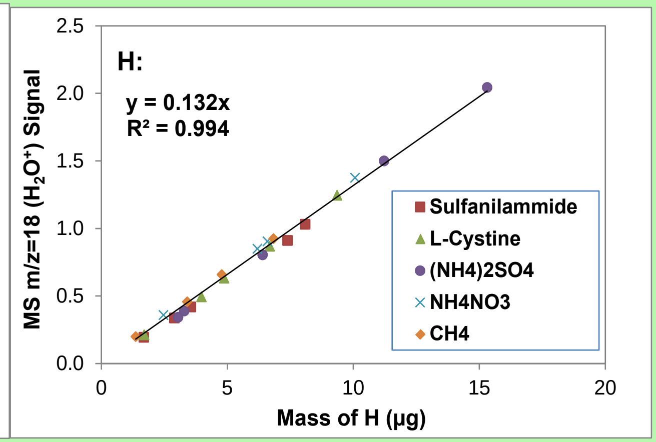


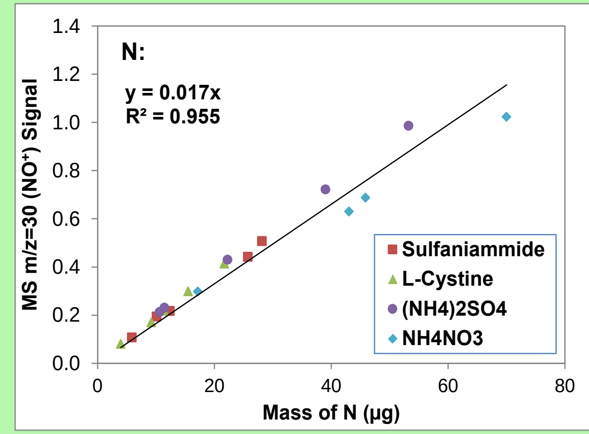


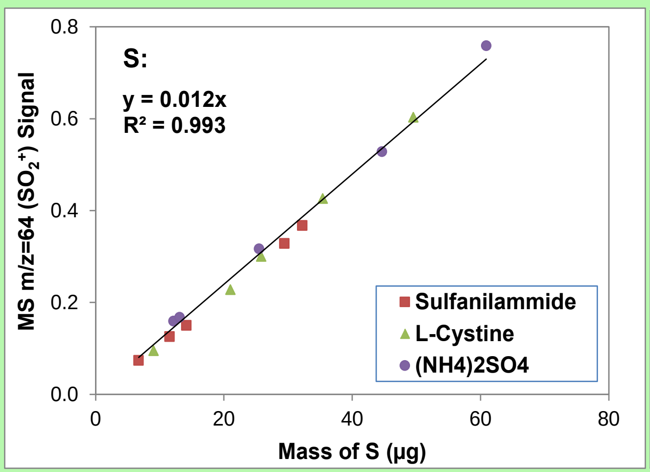
Fresno and Baltimore ambient samples (N=87)

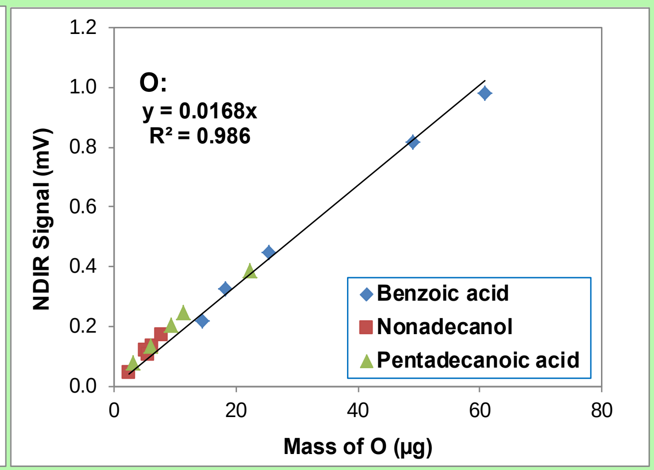
Instrument signals are linear with C, H, N, S, and O quantities for model compounds







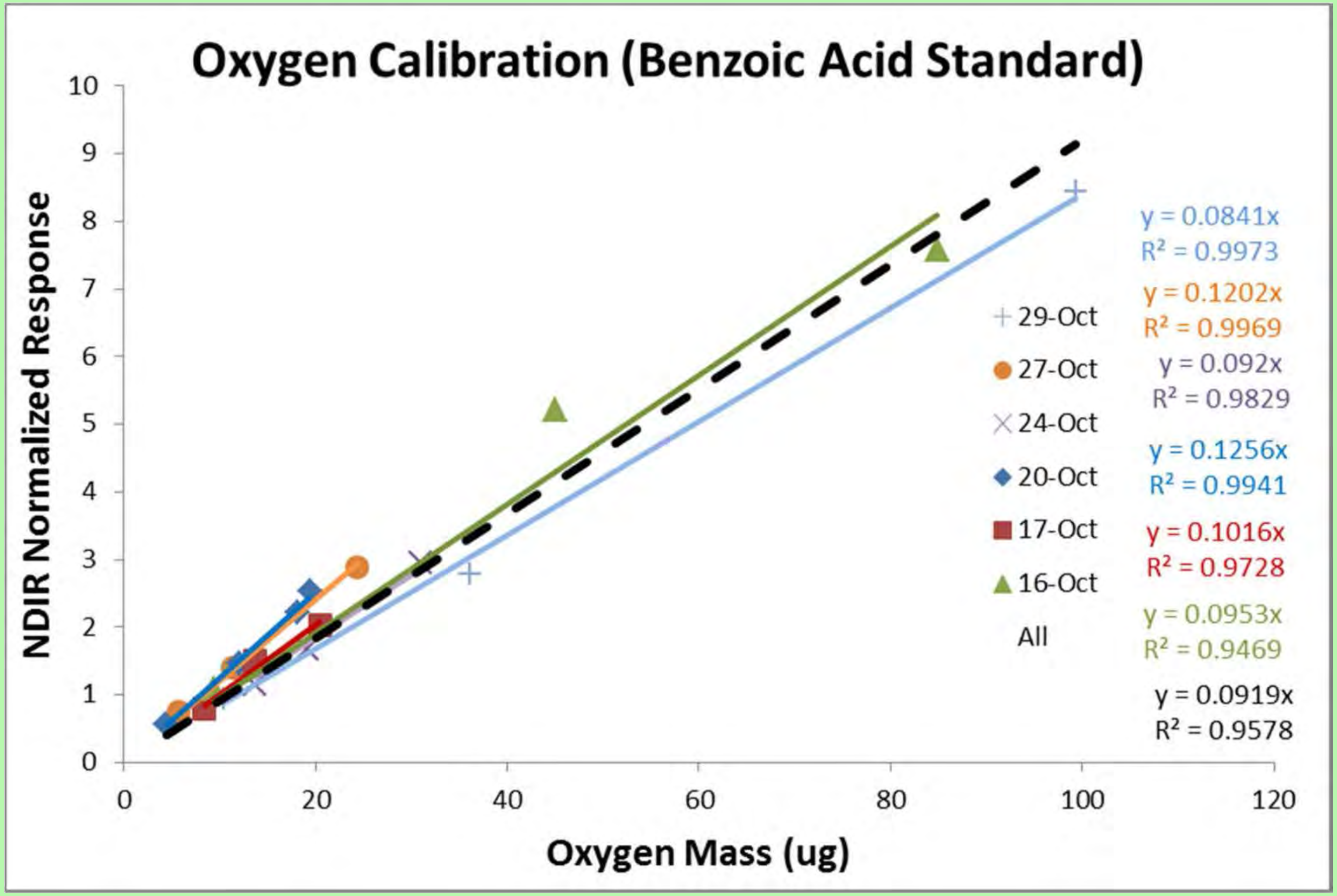




Calibration compounds:

- Ammonium nitrate: NH_4NO_3;
- Ammonium sulfate: $(NH_4)_2SO_4$;
- Benzoic acid: $C_7H_6O_2$;
- Carbon dioxide: CO_2;
- L-Cystine: $C_6H_{12}N_2O_4S_2$;
- Methane: CH_4;
- Nonadecanol: $C_{19}H_{40}O$;
- Pentadecanoic acid: $C_{15}H_{30}O_2$;
- Sulfanilamide: $C_6H_8N_2O_2S$

NDIR signal is linear with O quantities in calibrated chemicals

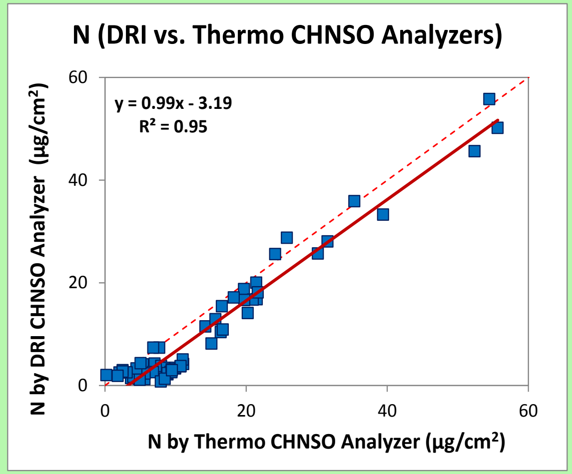


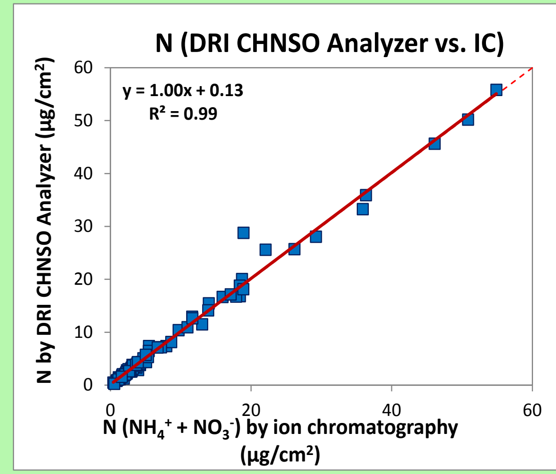
Challenges:

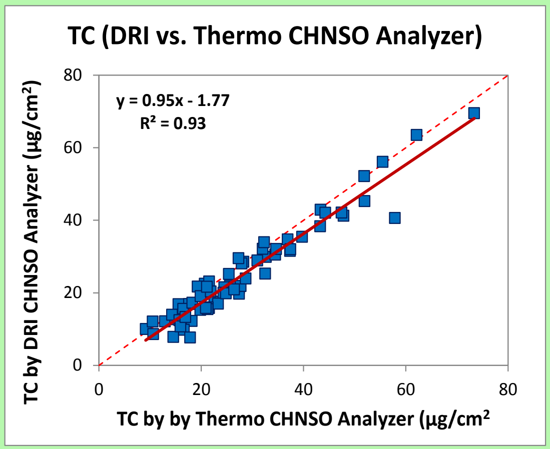
- **H_2O bound to filters and particles**
- **Intrusion of ambient O_2 into the analyzer**

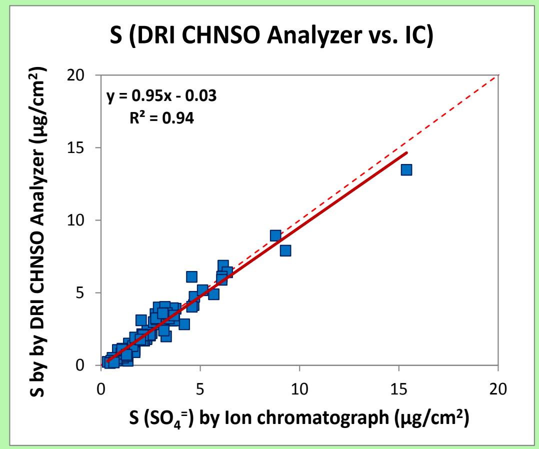
Benzoic acid: $C_7H_6O_2$;
Nonadecanol: $C_{19}H_{40}O$
Pentadecanoic acid: $C_{15}H_{30}O_2$

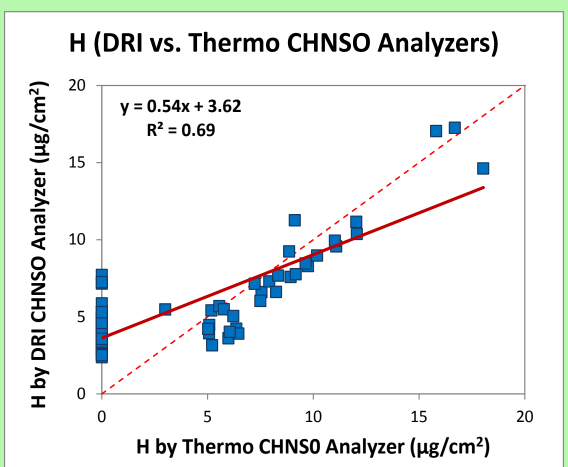
CHNSO concentrations are comparable with other methods

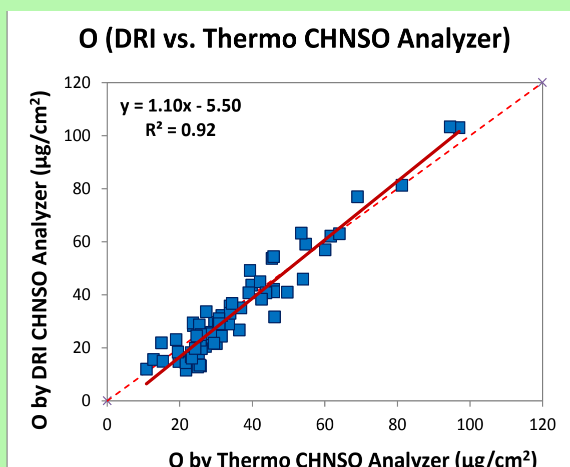








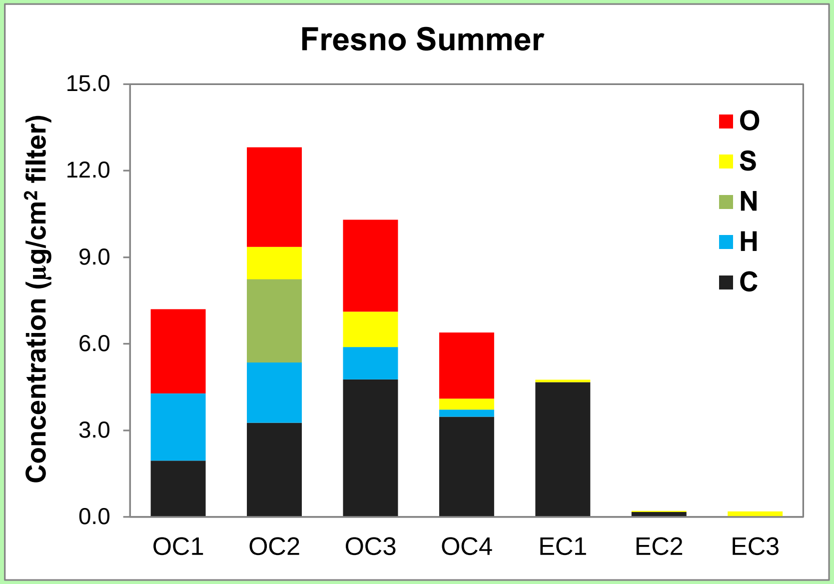


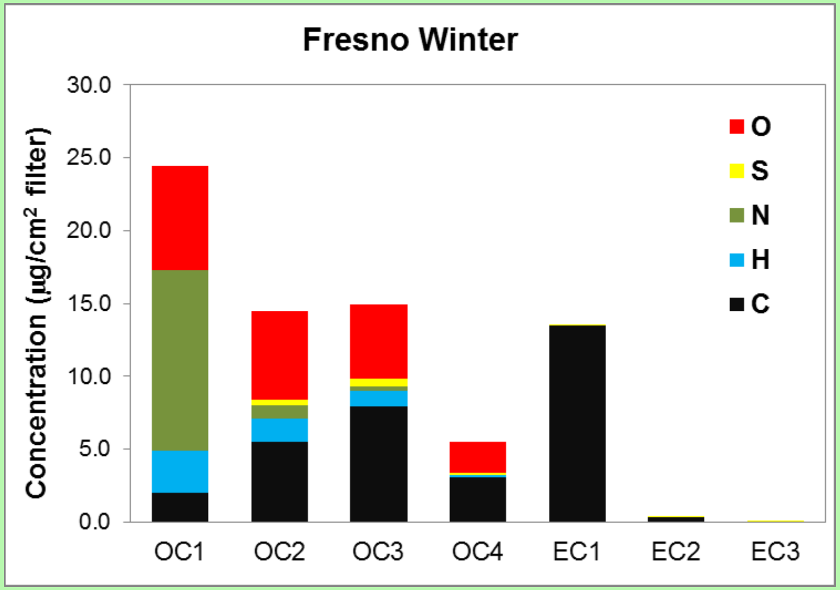


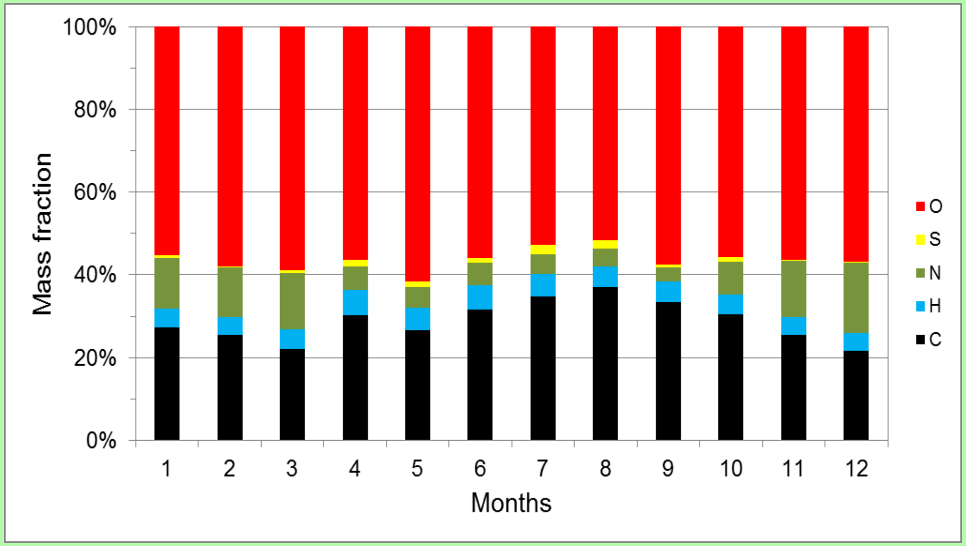
- **Thermo Flash EA1112 CHNS/O Analyzer**
- **Dionex Model ICS-3000 Ion Chromatographs (IC)**

Fresno and Baltimore ambient samples (N=87)

Composition varies between summer and winter
(Fresno, California)





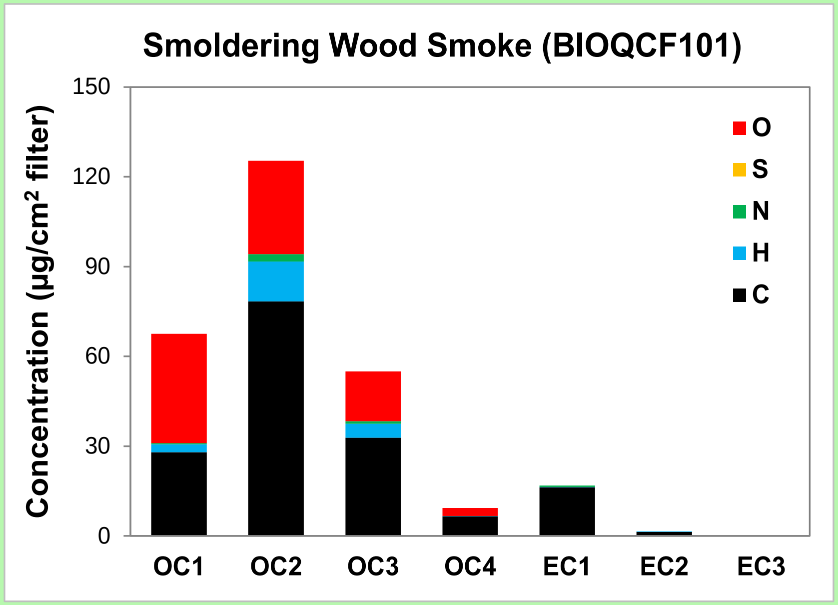


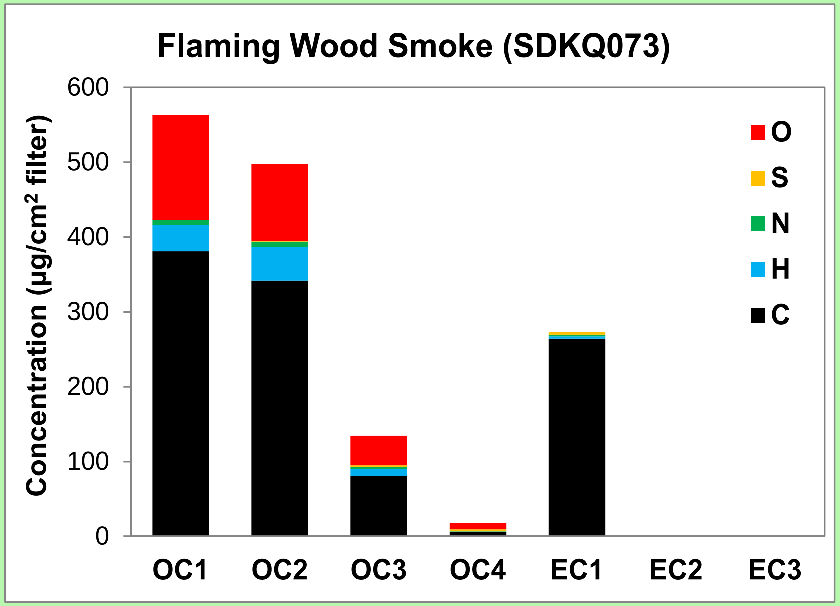
Seasonal variability in the CHNS-O composition of Fresno ambient samples (N = 67)

Abundant $(NH_4)_2SO_4$ in summer (Decompose at 200–400 °C; OC2 at 280 °C in 100% Helium) (EC/TC=0.23)

Abundant NH_4NO_3 in winter (Dissociation starts at room temperature; OC1 at 140 °C in 100% Helium) (EC/TC=0.28)

Source profiles vary between smoldering and flaming wood smoke for thermal carbon fractions





Smoldering wood smoke shows lower EC:TC and higher O:C ratios than flaming smoke.

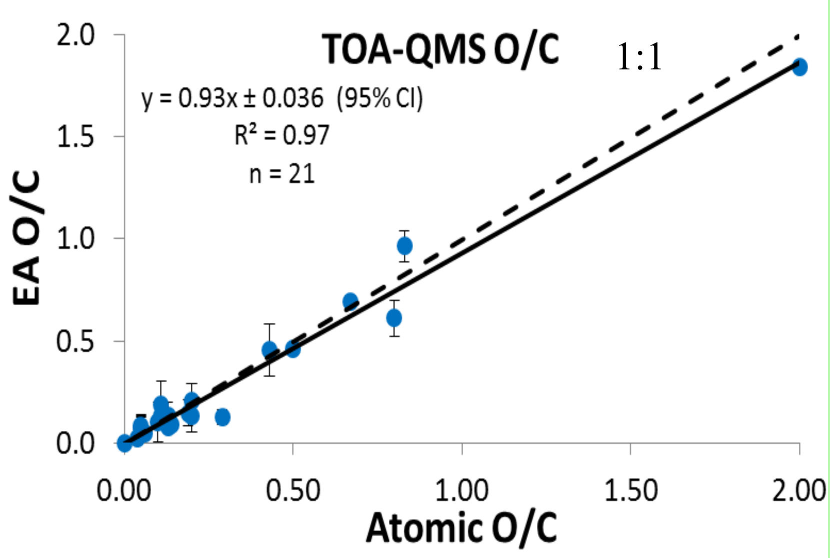
EC/TC=0.02

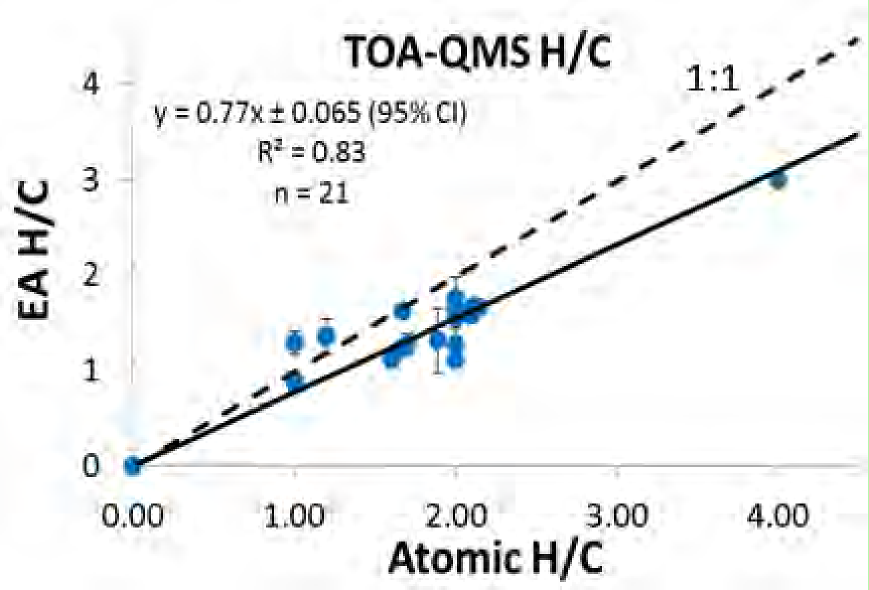
Fraction	Molar Ratios	
	H:C	O:C
OC	1.55	0.41
EC	0.93	NA
TC	1.54	0.40

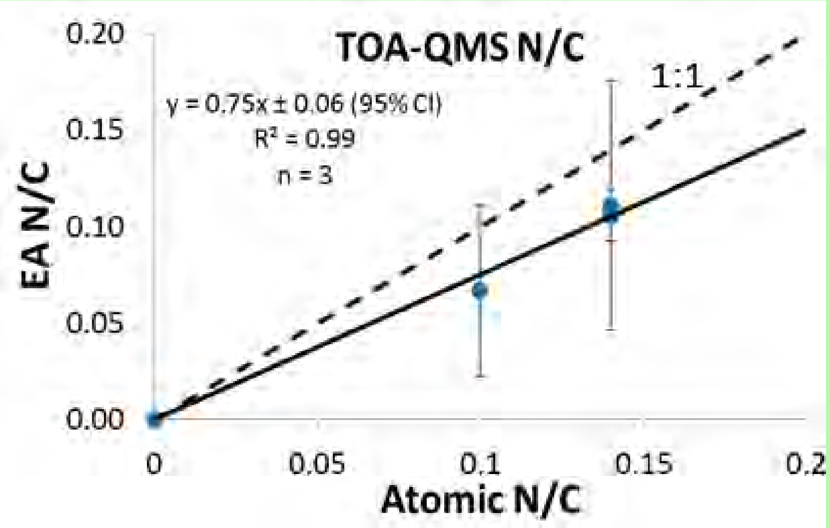
EC/TC=0.25

Fraction	Molar Ratios	
	H:C	O:C
OC	1.33	0.27
EC	0.14	NA
TC	1.04	0.20

Elemental analysis of organic standards shows consistent O/C and H/C relationships

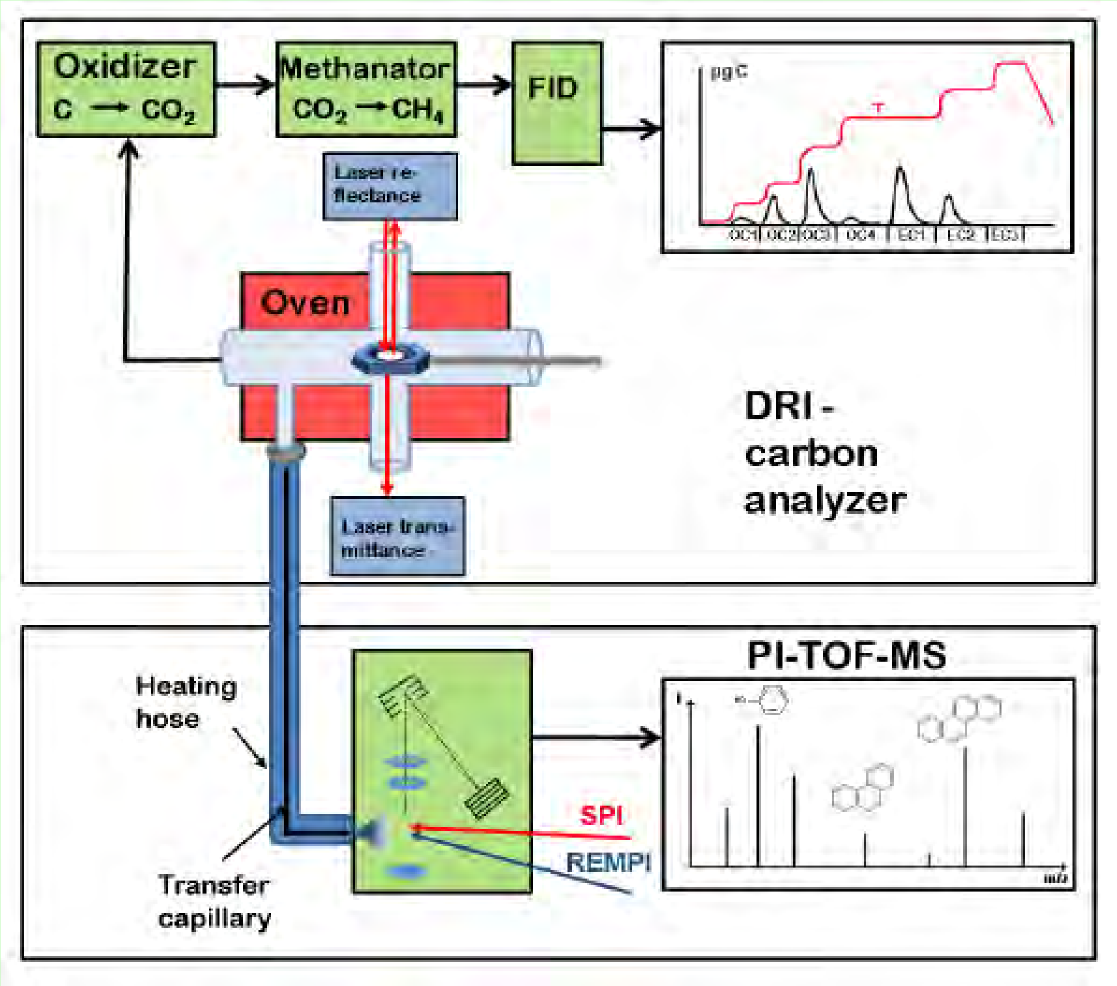




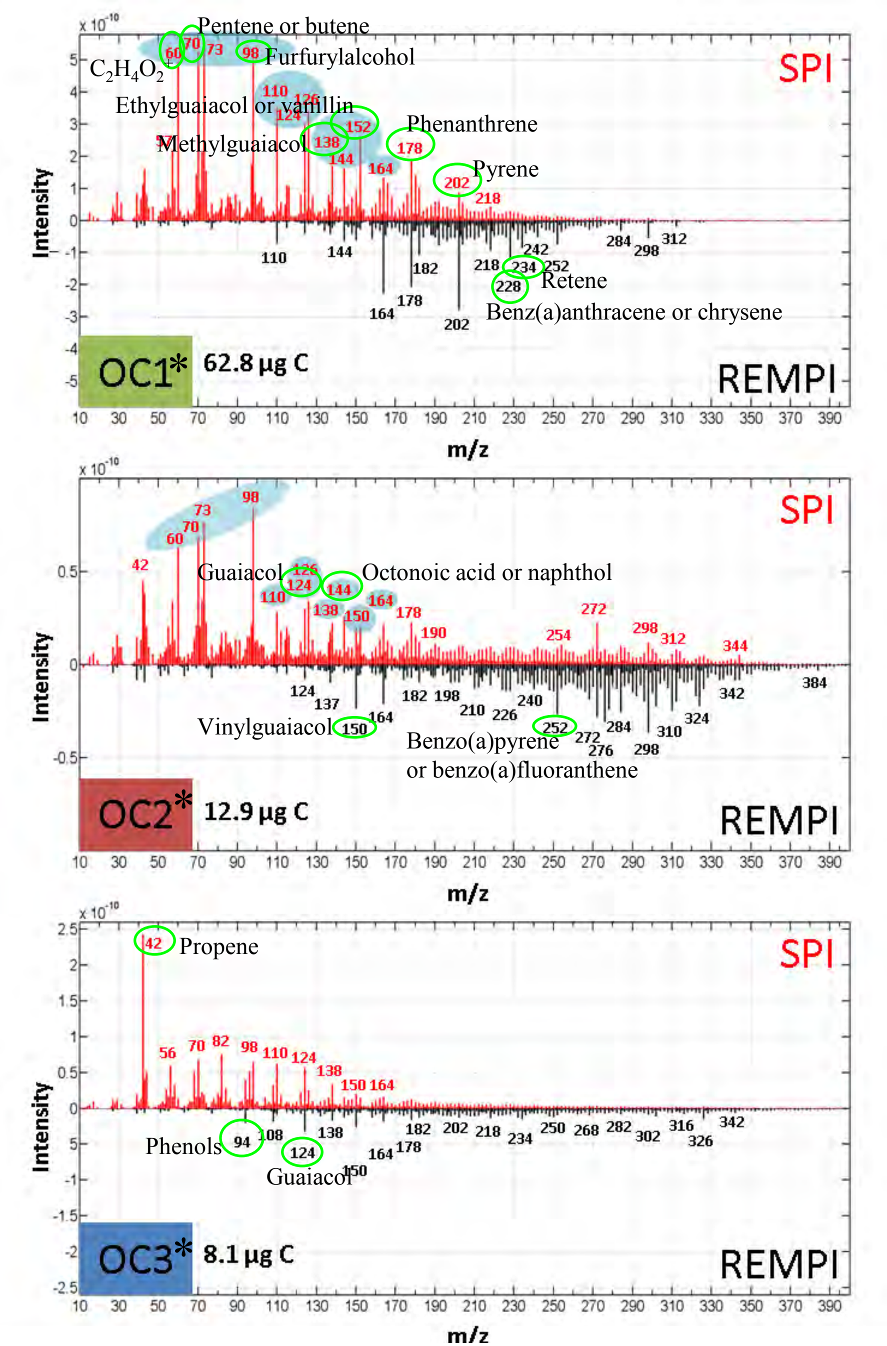


Lower N/C ratio may be due to inadequate number of samples and unaccounted N species

Approach 3: Detect thermal output with photon ionization time-of-flight mass spectrometry (TOA-PI-TOFMS)



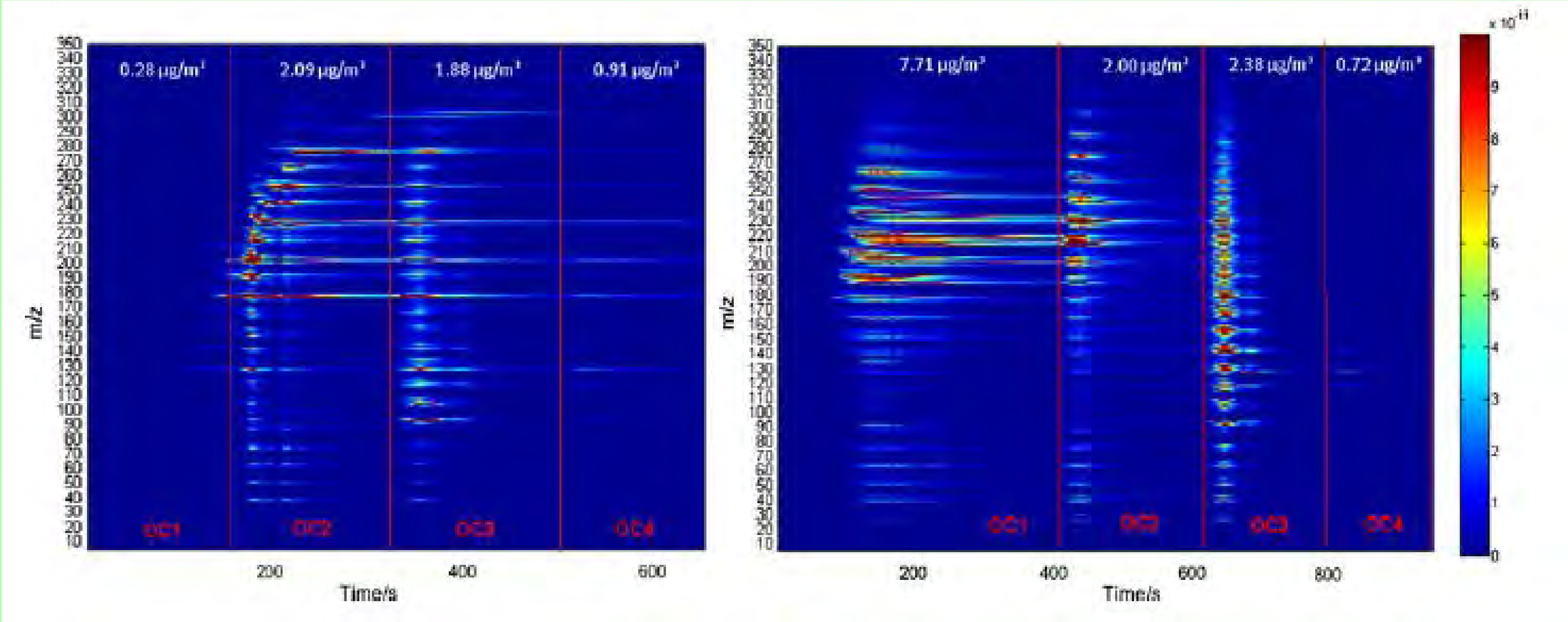
Diab et al. (2015). Hyphenation of a EC/OC thermal-optical carbon analyzer to photo ionization time-of-flight mass spectrometry: A new off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter. *Atmos. Meas. Tech. Discuss.*, (8):269-308.
Grabowsky et al. (2011). Hyphenation of a carbon analyzer to photo-ionization mass spectrometry to unravel the organic composition of particulate matter on a molecular level. *Anal. Bioanal. Chem.*, **401**(10):3153-3164.



Soft ionization doesn't fragment components, mass spectra are more complex, but individual compounds are quantified

*OC1-OC3 are OC fractions evolved at 140, 280, and 480°C in helium atmosphere following IMPROVE_A protocol

Distinct temperature/ion profiles are discernable, even without identifying individual compounds

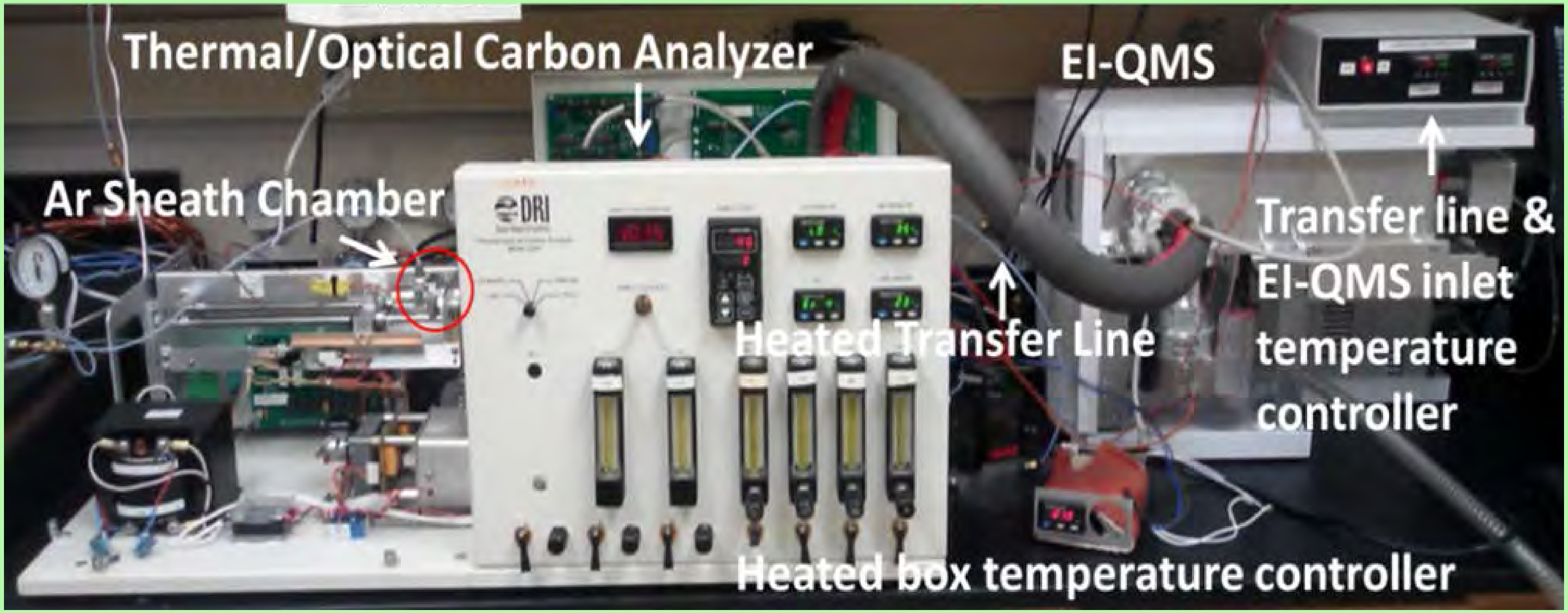


Gasoline Exhaust

Diesel Exhaust

Grabowsky et al. (2011). Hyphenation of a carbon analyzer to photo-ionization mass spectrometry to unravel the organic composition of particulate matter on a molecular level. *Anal. Bioanal. Chem.*, **401**(10):3153-3164.

These approaches seem to be feasible, but not yet practical



Approaches 1 and 2

Approach 3

Mini mass spectrometers are demonstrating sufficient sensitivity for ambient concentrations

Torion Technologies Inc.
American Fork, UT,
http://torion.com/home.html.

Microsaic Systems. Abingdon, UK,
http://www.microsaic.com/home/

Aston Labs, Purdue University, Lafayette, IN,
http://aston.chem.purdue.edu/research/instrumentation/miniature-mass-spectrometers.

Challenges for Enhanced Chemical Characterization of Filter Samples

- Perfecting, evaluating, and making more efficient procedures for additional characterization
- Modifying instrumentation and procedures to incorporate more specific analyses methods into long-term chemical speciation networks to obtain more information from existing samples
- Maintaining continuity and consistency with the long-term trends data sets
- Developing more detailed source profiles with these methods for speciated inventories and source apportionment

Acknowledgements

- U.S. National Science Foundation (CHE 1214163)
- National Park Service IMPROVE Carbon Analysis Project (C2350000894)